# Evaluation of S, S, S-Tributyl Phosphorotrithioate (DEF) As a Toxic Air Contaminant

Part B
Exposure Assessment

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Public Exposure to Airborne S, S, S-Tributyl Phosphorotrithioate (DEF) in California HS-1712

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#### **SUMMARY**

DEF is a cotton defoliant that is applied mainly by air in California. The use report data suggest that the use of DEF in California has been steady, ranging from approximately 750,000 to 1,000,000 lb each year. Residents of rural communities in the proximity of cotton fields treated with DEF are potentially exposed to airborne residues during the application and harvest seasons. There have been numerous complaints of human illness that were linked to DEF in the past, but the number of DEF-associated illness cases reported by physicians averaged less than two cases per year from 1982 to 1991. The reported illness cases are mostly occupational and occurred during handling of DEF products.

This document is a quantitative assessment of public exposure to airborne DEF and is prepared as Part B of the evaluation of DEF as a possible toxic air contaminant (TAC) under the requirements of Assembly Bill 1807. Monitoring data from ambient air in residential areas in interface with cotton growing regions of California that were discussed in Part A (Environmental Fate) of the evaluation of DEF as a possible TAC were used in this document to estimate public exposure. DEF was detected in the ambient air during September and October, coinciding with its application and cotton harvest season. Its concentrations peaked during mid-September to mid-October. DEF concentrations were much higher in the ambient air of the monitored rural areas than in that of the monitored urban areas. Short-term (daily), intermediate (seasonal), and long-term (annual) exposures of children, adult males, and adult females living in rural and urban areas close to cotton fields were estimated based on the concentrations of the DEF in the ambient air and the inhalation rates for each subgroup during various activities. According to these estimates, children have the highest potential exposure per unit (kg) of body weight followed by adult males and adult females. The highest absorbed daily dosages for children, adult males, and adult females were 304, 126, and 94 ng/kg/day, respectively. The highest annual average daily dosages for children, adult males, and adult females were 20, 8, and 6 ng/kg/day, respectively.

## I. INTRODUCTION

DEF® and Folex® are the trade names for S,S,S-tributyl phosphorotrithioate  $((C_4H_9S)_3P=0, CAS # 78-48-8)$ . The name "DEF" is used throughout this document in reference to the active ingredient S, S, S-tributyl phosphorotrithioate. n-Butyl mercaptan is a degradation product of DEF, n-Butyl mercaptan is a colorless liquid with a strong skunk-like odor. It is highly volatile with a vapor pressure of 35 mm Hg at 20°C (GPC, 1982). DEF has a vapor pressure of 6.5 x 10<sup>-6</sup> mm Hg at 25°C (Tallott and Mosier, 1987). DEF is a pesticide used for cotton defoliation and applied mostly by air in California. Air monitoring studies showed DEF in the ambient air of residential cotton growing areas. Thus, residents of cotton growing areas in California are potentially exposed to DEF in the ambient air. DEF inhalation has caused adverse acute and subchronic effects in laboratory rats. In 1983, the California Legislature signed Assembly Bill 1807 into law. Assembly Bill 1807 requires the Department of Pesticide Regulation to determine pesticides qualifying as toxic air contaminants (TAC). The evaluation of DEF as a possible TAC consists of three parts. Part A is the environmental fate of DEF. Part C is the health assessment of DEF. This part is a quantitative assessment of public exposure to airborne DEF, and is prepared as Part B of the evaluation of DEF as a possible TAC. The assessment of occupational exposure to DEF is not included in this document. California has other laws and regulations that govern occupational health and safety.

## II. SOURCES OF ATMOSPHERIC DEF IN CALIFORNIA

## A. Products

To date, there are two DEF-containing pesticide products registered in California. They are DEF $^{\circledR}$  6 Emulsifiable Defoliant and Folex $^{\circledR}$  6 EC Cotton Defoliant. Both products are emulsifiable concentrates, each containing 70.5% active ingredient (a.i.) which is equivalent to 6 lb/gal.

## B. Usage

DEF is used exclusively for cotton defoliation in California. The recommended application rate is 0.75 to 1.9 lb a.i./acre. According to label directions, DEF can be applied as a dilute spray in 5 to 10 gal. of water per acre by air or 15 to 25 gal. of water per acre with ground equipment. It can not be used through any type of irrigation system. DEF is applied predominantly by air in California.

During 1992, over 6,250 applications were made to 574,170 acres of cotton fields in California using 789,800 lb of DEF (DPR, 1994). The DEF use trend in California is illustrated in Figure 1.

Cotton defoliation is a seasonal activity in California. It starts in early September (Southern San Joaquin Valley) and ends in mid-October (Central San Joaquin Valley), depending on weather conditions and crop maturity (Vargas, 1993; Wright, 1993, telephone communication). According to the product label, DEF effectiveness is limited by temperature. The climatic conditions favorable for effective use of DEF normally occur during the first two to three weeks of the defoliation season (Wright, 1993, telephone communication). In 1992 to 1995, more than 80% of total DEF use each year in California was applied in Fresno, Kern, and Kings counties (Table 1). The use in Fresno county alone accounted for approximately 50% of the total use.

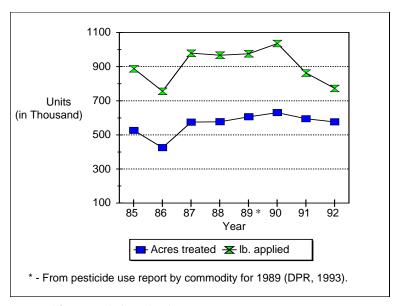


Figure 1. DEF Use and Area Treated During 1985 to 1992 in California<sup>a</sup>.

a - After DPR, 1987 to 1994

## III. PUBLIC EXPOSURE TO DEF IN THE AMBIENT AIR OF CALIFORNIA

Residents of rural communities in the proximity of cotton fields treated with DEF are potentially exposed to airborne residues during the application and harvest seasons. In 1978, California adopted the regulation prohibiting applications of DEF closer than 1/2 mile to zoned residential areas where people are actually residing, any inhabited residential area designated by the agricultural commissioner, or any school in session or due to be in session within 24 hours (California Code of Regulations (CCR), Title 3, Section 6470). The regulations also require that applications must not in any case be made within 1/8 mile of any school. In 1984, California

adopted the regulation requiring that the level of n-butyl mercaptan in DEF-formulated products not exceed 0.1% (CCR, Title 3, Section 6361).

Table 1. Counties Applying DEF in 1992–1995 and Their Total Populations in 1990.

County	1992 Amount applied, lb <sup>a</sup> (%)	1993 Amount applied, lb (%)	1994 Amount applied, lb (%)	1995 Amount applied, lb (%)	Total population <sup>b</sup>
Colusa	— (—)	— (—)	562 (< 0.1)	2,535 (< 0.1)	16,275
Fresno	397,147 (51.6)	477,844 (48.8)	451,384 (49.4)	436,936 (49.5)	667,490
Glenn	— (—)	— (—)	— (—)	83 (< 0.1)	24,798
Imperial	10,079 (1.3)	7,578 (0.7)	8,952 (< 0.1)	7,621 (< 0.1)	109,305
Kern	110,926 (14.4)	120,111 (12.3)	118,348 (13.0)	90,425 (10.2)	543,477
Kings	102,595 (13.3)	199,755 (20.4)	198,894 (21.8)	185,354 (21.0)	101,469
Madera	37,739 (4.9)	44,557 (4.6)	33,345 (3.7)	34,555 (3.9)	88,090
Merced	70,579 (9.2)	79,939 (8.2)	73,376 (8.0)	84,584 (9.6)	178,403
Riverside	11,602 (1.5)	9,886 (1.0)	9,080 (1.0)	11,151 (1.3)	1,170,413
San Bernard	lino 503 (< 0.1)	462 (< 0.1)	650 (< 0.1)	325 (< 0.1)	1,418,380
Stanislaus	15 (< 0.1)	— (—)	— (—)	102 (< 0.1)	370,522
Tulare	28,333 (3.7)	38,765 (4.0)	19,034 (2.1)	29,373 (3.3)	311,921
Yolo	— (—)	17 (< 0.1)	— (—)	524 (< 0.1)	141,092
Total	769,518 (100.0)	978,914 (100.0)	913,625 (100.0)	883,567(100.0)	

a 1 pound (lb) = 0.4535 kg

#### IV. HUMAN ILLNESSES ASSOCIATED WITH DEF

California Health and Safety Code requires that any illness suspected of being caused by a pesticide be reported by the examining physician to the county health officer within 24 hours (CCR, Title 17, Section 2950). There were a total of 16 illness and injury cases associated with exposure to DEF and DEF in combination with other pesticides in California from 1982 through 1991 (DPR, 1994). These cases were mostly due to occupational exposure (12 occupational and 4 non-occupational cases) and resulted from close contact with DEF products. Of the 16 cases, 11 were systemic illnesses, two were eye injuries, and three were respiratory illnesses. Systemic poisoning due to exposure to DEF and DEF in combination with other pesticides was positively identified (definite) in four cases. Cholinesterase depression was observed in three of the four definite systemic cases. One systemic case was classified as probable and six others as possible cause of acute poisoning.

<sup>&</sup>lt;sup>b</sup> Population totals from the 1990 U.S. Census

In a 1977 report from the California Department of Food and Agriculture, several hundred complaints of human illness were summarized (Maddy and Peoples, 1977). The illnesses were characterized by wheezing, coughing, nausea, and other discomforts that could be linked to the foul odor of n-butyl mercaptan, a degradation product of the cotton defoliant. Due to improvements in the manufacturing process of DEF, a very low odor formulation was made available which, to some extent, minimized the odorous problem associated with the use of this cotton defoliant. However, this report also emphasized that after the low-odor cotton defoliant has been sprayed on to the field, foul odorous material is generated and may persist for up to 48 hours due to photo-degradation and other environmental conditions (Maddy and Peoples, 1977). Thus, removing the impurities of the defoliant product alone did not totally eliminate the foul odor.

An article entitled "Merphos Poisoning or Mass Panic?" reported a chemical spillage in a ship in Mexico on route to Sydney, Australia (McLeod, 1975). Six hundred and forty-three exposed persons were seen at a local hospital. The most serious problem appeared to be the inhalation toxicity of the n-butyl mercaptan. It was estimated that the airborne concentration of n-butyl mercaptan exceeded 0.5 ppm, and in some situations, it had exceeded 10 ppm (American Conference of Governmental Industrial Hygienists {ACGIH} TLV for n-butyl mercaptan is 0.5 ppm time weighted average). Reportedly, there was no cholinesterase inhibition in the tested individuals. In addition to the symptoms usually seen with exposure to n-butyl mercaptan, the author emphasized that panic, fear, anxiety, and exhaustion played a major role in exhibiting or intensifying some of the symptoms. Since caustic soda was used for the decontamination process of the chemical spillage, more n-butyl mercaptan was generated, thus, resulting in the continuous supply of foul odorous chemical. The author concluded that there was no significant human illness resulting from organophosphate poisoning in this episode.

Kilgore *et al.*(1984) conducted medical examinations and psychological testing of 14 aerial applicator personnel who were exposed to DEF. These volunteers were pilots, flaggers, mixer/loaders and other personnel. Medical examination included a general physical examination, chest X-ray, EKG, total and RBC cholinesterase, blood chemistry, and urinalysis. There were no significant medical findings noted in any of the 14 workers. A battery of psychological tests were utilized to measure the neuropsychological functions of the exposed persons. These particular measures were selected because they were considered to be measures of subtle organic brain dysfunction. The tests found no significant differences between the preand post-exposure scores on any of the psychological measures utilized.

An epidemiological study was conducted by the Department of Health Services on acute health effects associated with the exposure to cotton defoliants (Scarborough *et al.*, 1989). DEF was the focus of this study. The survey was conducted by phoning 460 residents of agricultural communities in the San Joaquin Valley during cotton defoliation season. Scarborough *et al.* 

found that a positive association exists between the various symptoms and spraying of cotton defoliants for people living or working near a sprayed field. These symptoms included "respiratory allergy", eye irritation, rhinitis, throat irritation, shortness of breath, wheezing, "asthma symptoms", nausea, and diarrhea. In this epidemiological survey, it was not reported whether the regulation requiring a 1/2 mile buffer zone between residential areas and the sprayed fields had been enforced during DEF applications.

Although very low exposure to DEF is unlikely to cause a toxicological effect, the presence of a minute amount of the degradative product (n-butyl mercaptan) causing foul odor is likely to be associated with the various subjective symptoms and complaints. The TLV - TWA for n-butyl mercaptan is 0.5 ppm which indicates exposure at this level should not result in untoward acute health effects (ACGIH, 1988). However, the offensive odor which can be detected at 0.001 ppm (Amoore and Hautala, 1983) may have caused the various discomforts and reported illnesses.

## V. DEF CONCENTRATION IN THE AMBIENT AIR OF CALIFORNIA

There are several studies during which downwind drift of DEF from the application sites and/or ambient air in residential rural areas nearby cotton fields or cities in cotton growing areas were monitored. Part A of this document contains detailed discussions of these studies. Monitoring data from ambient air in residential areas in interface with cotton growing regions of California were selected to estimate public exposure to DEF.

Stanley *et al.* (1971) found DEF in the ambient air of Stoneville, MS (average =  $16.0 \text{ ng/m}^3$ ) during May through October. They did not detect DEF in the ambient air of urban Fresno, or Riverside, CA. Arthur *et al.* (1976) detected DEF at a maximum concentration of  $16.0 \text{ ng/m}^3$  during September and October in Stoneville, MS.

In ambient air monitoring studies conducted in residential areas in California, Oshima *et al.* (1980) did not detect DEF on XAD-4 resin samples collected in two schools, one in Mendota (Sept. 25 to Oct. 23, 1979) and one in Dos Palos (Oct. 1 to Oct. 23, 1979). The Meloy Industries Total Sulfur Analyzer (MITSA) used in the same study detected some gas-phase sulfur-containing compounds. The analysis by MITSA is not specific to DEF or its degradation products such as n-butyl mercaptan and dibutyl disulfide to determine the level of these compounds.

A CDFA study (1981) monitored ambient air for DEF and n-butyl mercaptan in Coalinga, Dos Palos, Lemoore, and Mendota from October 1 through November 2, 1980. All applications within one mile of these monitoring sites were made using ground equipment except in Mendota where aerial applications were made nearby. The information from this study was

presented in an executive summary. Information such as MDL, type of the sampling media, and efficiency of the sampling media was missing, and only positive samples for n-butyl mercaptan concentrations were reported. DEF concentration ranged from non-detectable to  $0.4 \text{ ng/m}^3$ . Only 6% (29/480) of the samples taken and analyzed instantly were positive for n-butyl mercaptan. Daily average concentration of n-butyl mercaptan for positive samples ranged from  $1.9 \,\mu\text{g/m}^3$  to  $28.6 \,\mu\text{g/m}^3$ . n-Butyl mercaptan concentration showed no clear pattern over time either in a single location (Dos Palos) or in all locations combined.

Table 2. n-Butyl Mercaptan Concentration ( $\mu g/m^3$ ) in Ambient Air from October 1 to November 2, 1980 in Coalinga, Dos Palos, Lemoore, and Mendota<sup>a</sup>.

Monitoring Site	Date	Daily Average Concentration
Coalinga	10/03/80	23.6
Dos Palos	10/04/80	5.1
Dos Palos	10/05/80	2.7
Lemoore	10/07/80	8.1
Lemoore	10/08/80	1.9
Mendota	10/23/80	22.5
Dos Palos	10/26/80	7.2
Dos Palos	10/29/80	28.6
	Coalinga Dos Palos Dos Palos Lemoore Lemoore Mendota Dos Palos	Coalinga 10/03/80 Dos Palos 10/04/80 Dos Palos 10/05/80 Lemoore 10/07/80 Lemoore 10/08/80 Mendota 10/23/80 Dos Palos 10/26/80

a - After CDFA, 1981, Positive samples only.

Seiber *et al.* (1988) monitored ambient air of four rural areas in Fresno County (Tranquility, San Joaquin, Five Points, and Huron) and two urban background locations in the cities of Fresno and Bakersfield from August 31 through November 4, 1987. The four rural locations were in the proximity of cotton fields ranging from 10 to 400 meters from the edges of the fields. High volume air samplers equipped with XAD-4 resin sampling tubes were used. Figure 2 illustrates DEF concentration pattern in the ambient air at the rural locations during the season. Lower levels of DEF were detected at all four locations during the period of August 31 through the first week of September. Residue levels peaked between mid-September and mid-October and started declining in mid-October reaching lower levels during late October and early November. No DEF residues were detected (MDL = 1.1 ng/m<sup>3</sup>) at the urban sites except for two days in Bakersfield and four days in Fresno where the DEF concentrations were slightly above the MDL (2.3 to 12.0 ng/m<sup>3</sup>).

No field-spiked samples were prepared during the study. The samples were placed on dry ice in the field and in a freezer (-4 °C or lower) at the lab and stored no more than two weeks before analysis. Samples spiked in the lab and stored for two weeks at -4 °C before analysis produced an average recovery of 96%. Trapping efficiency for the spiked samples was 62%. The data in Table 2 are the average of two or three replicate samples.

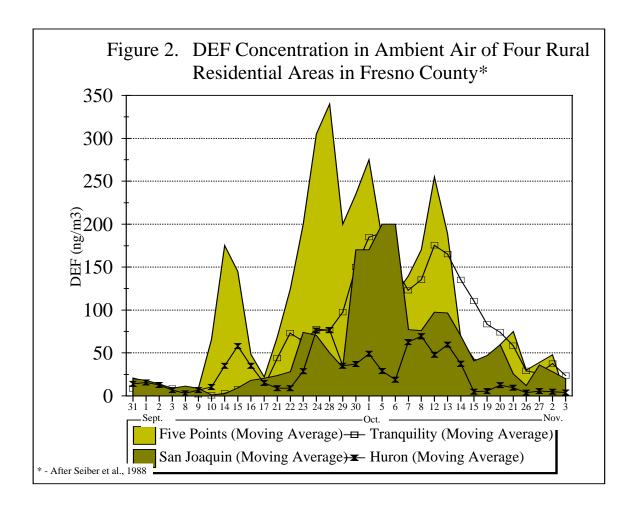


Table 3. DEF Concentration (ng/m³) in Ambient Air of Four Rural Areas in Fresno County During the 1987 Cotton Defoliation Season<sup>a</sup>.

Cou	nty During the 19				
Date	Five Points	Tranquility	San Joaquin	Huron	Average
August 31	21.0	8.4	20.0	14.0	16
September 1	13.0	7.7	16.0	17.0	13
2	10.0	12.0	11.0	8.7	11
3	2.7	4.7	6.6	4.7	5
8	16.0	3.2	16.0	1.2	9
9	1.8	N/Db	1.7	12.0	4
10	130.0	N/D <sup>b</sup>	N/D <sup>b</sup>	8.7	35
14	220.0	5.3	4.4	61.0	73
15	70.0	9.9	14.0	55.0	37
16	27.0	9.9	22.0	15.0	18
17	17.0	12.0	19.0	15.0	16
21	120.0	76.0	28.0	3.1	57
22	130.0	70.0	no data	15.0	72
23	270.0	57.0	74.0	42.0	111
24	340.0	98.0	67.0	110.0	154
28	no data	55.0	33.0	43.0	44
29	200.0	140.0	no data	27.0	122
30	270.0	160.0	170.0	47.0	162
October 1	280.0	210.0	no data	51.0	180
5	86.0	170.0	200.0	6.8	116
6	150.0	126.0	no data	31.0	102
7	130.0	120.0	77.0	94.0	105
8	210.0	151.0	75.0	45.0	120
12	300.0	200.0	120.0	51.0	168
13	78.0	130.0	73.0	68.0	87
14	55.0	140.0	67.0	6.9	67
15	31.0	81.0	14.0	2.8	32
19	45.0	86.0	80.0	8.1	55
20	75.0	62.0	39.0	17.0	48
21	no data	55.0	12.0	2.1	23
26	30.0	3.5	no data	5.4	13
27	48.0	49.0	36.0	5.7	35
November 2	10.0	26.0	20.0	4.0	17
3		21.0	20.0	1.0	1,
3		21.0			
Highest	340.0	210.0	200.0	110.0	180.0
Arithmetic Mean	113.0	69.4	47.0	27.2	64.4
Arithmetic SD	101.0	63.1	48.8	27.3	52.3
	101.0	03.1	10.0	27.3	52.5
Highest <sup>C</sup>	548.0	339.0	321.0	177.0	294.0
Arithmetic Mean <sup>c</sup>	182.0	112.0	75.8	43.9	104.0
Arithmetic SD <sup>C</sup>	163.0	102.0	78.7	44.1	84.3
	100.0	102.0	,		0

a - After Seiber et al., 1988.

b - Non-detectable - Used 1/2 MDL, (MDL=1.1 ng/m3).

c - Corrected for 62% trapping efficiency.

SD - Standard deviation

Kilgore *et al.* (1984) monitored ambient air once each time during preapplication, peak application, one week after peak application, and several weeks after the peak application season in ten locations in rural and urban cotton-growing areas of Kern County. Sampling was conducted twice for three hours each time. Samples were collected on a glass fiber filter backed by a XAD-4 resin filter. DEF recoveries from spiked glass fiber and XAD-4 resin filters were 95% and 99%, respectively. Simulated field recoveries of DEF from glass fiber and XAD-4 resin filters combined averaged 80%. No DEF was detected during pre-application (mid September) at these locations except in Delano and Shafter where DEF was detected at 3.6 ng/m<sup>3</sup> and 5.4 ng/m<sup>3</sup>, respectively due to early applications in these areas. DEF levels during peak application season in early October and one week after the peak application season are presented in Tables 3 and 4, respectively. DEF was detected at all ten locations during peak application season. The highest DEF level was 57.1 ng/m<sup>3</sup>, at Lerdo Prison during the evening (p.m.) and the lowest levels were 4.1 ng/m<sup>3</sup>, at both south and west Bakersfield during the evening. Mean DEF level during the evening hours.

Table 4. DEF Concentration (ng/m<sup>3</sup>) During Peak Application Season (Early October) in Ten Locations in Kern County<sup>a</sup>.

Location	a.m. Fb	a.m. R <sup>b</sup>	p.m. Fb	p.m. R <sup>b</sup>	a.m. total	p.m. total	a.m. Total <sup>d</sup>	p.m. Total <sup>d</sup>
Delano	4.5	10.7	24.1	16.1	15.2	40.2	19.0	50.3
Wasco	45.5	4.5	17.8	N/D <sup>c</sup>	50.0	19.2	62.5	24.0
Shafter	7.1	42.8	2.7	16.9	49.9	19.6	62.4	24.5
Lerdo Prison	19.6	16.1	51.7	5.4	35.7	57.1	44.6	71.4
Taft	3.6	3.6	8.0	3.6	7.2	11.6	9.0	14.5
Arvin	3.6	3.6	4.5	12.5	7.2	17.0	9.0	21.3
Bakersfield E.	25.0	14.3	7.1	3.6	39.3	10.7	49.1	13.4
Bakersfield C.	5.4	36.6	12.5	N/D <sup>c</sup>	42.0	13.9	52.5	17.4
Bakersfield S.	48.2	6.2	2.7	N/D <sup>c</sup>	54.4	4.1	68.0	5.1
Bakersfield W.	22.3	6.2	2.7	N/D <sup>c</sup>	28.5	4.1	35.6	5.1
Highest	48.2	42.8	51.7	16.9	54.4	57.1	68.0	71.4
Mean*	18.5	14.4	13.4	6.4	32.9	19.8	41.2	24.7
$SD^*$	16.2	13.3	14.5	6.0	16.8	15.8	21.0	19.7

a - From Kilgore et al., 1984.

b - F = Glass fiber; R = XAD-4 resin

c - Non-detectable- used 1/2 MDL, (MDL=2.7 ng/m<sup>3</sup>).

d - Corrected for 80% field recoveries.

<sup>\* -</sup> Arithmetic

Due to analytical problems, no readings were available for Lerdo Prison one week after the peak application season (Table 4). Average morning DEF concentration declined from 32.9 ng/m³ (Table 3) during the peak application season to 22.8 ng/m³ (Table 4) one week after the peak application season. Average evening concentrations during and one week after the peak application season showed no significant change, primarily due to an evening high reading (87.4 ng/m³) in Shafter. This evening high reading is also the highest concentration recorded for the season. Bakersfield locations had the lowest levels. About two weeks after the application season ended and well into cotton harvesting season in early November, no DEF was detected at any locations except at one sample in Taft at the MDL.

Table 5. DEF Concentration (ng/m<sup>3</sup>) One Week After Peak Application (mid-October) in Ten Locations in Kern County<sup>a</sup>.

Location	a.m. F <sup>b</sup>	a.m. R <sup>b</sup>	p.m. F <sup>b</sup>	p.m. R <sup>b</sup>	a.m. total	p.m. total	a.m. Total <sup>d</sup>	p.m. Total <sup>d</sup>
Delano	11.6	N/D <sup>c</sup>	5.6	N/D <sup>c</sup>	13.0	7.0	16.3	8.8
Wasco	16.1	5.4	14.3	N/D <sup>c</sup>	21.5	15.7	26.9	19.6
Shafter	22.3	6.2	87.4	15.2	28.5	103.0	35.6	128.0
Lerdo Prison	no data	no data	no data	no data	no data	no data	no data	no data
Taft	10.7	N/D <sup>c</sup>	25.9	N/D <sup>c</sup>	12.1	27.3	15.1	34.1
Arvin	no data	no data	7.1	3.6	no data	10.7	no data	13.4
Bakersfield E.	16.1	N/D <sup>c</sup>	2.7	N/D <sup>c</sup>	17.5	4.1	21.9	5.1
Bakersfield C.	9.8	12.5	2.7	3.6	22.3	6.3	27.9	7.9
Bakersfield S.	23.2	19.6	7.1	N/Dc	42.8	8.5	53.5	10.6
Bakersfield W.	18.7	6.2	4.5	N/Dc	24.9	5.9	31.1	7.4
Highest	23.2	19.6	87.4	15.5	42.8	103.0	53.5	128.0
Mean*	16.1	6.8	17.5	3.4	22.8	20.9	28.5	26.1
$\mathrm{SD}^*$	4.8	6.0	25.7	4.3	9.2	29.7	11.5	37.1

a - From Kilgore et al., 1984.

The earlier monitoring data (Stanley, et al., 1971; Oshima, et al., 1980; CDFA, 1981) either detected low or no concentrations of DEF in the ambient air of residential areas in California. In some instances they reported only the positive results or the MDL was missing. The analysis for n-butyl mercaptan in the CDFA study was compound specific and the results are indicative of the levels of n-butyl mercaptan in the ambient air of tested sites. However, the CDFA study concluded that the results of DEF and n-butyl mercaptan monitoring in the study may be uncharacteristic of short term exposure because of the time of application and the relative

b - F = Glass fiber; R = XAD-4 resin

c - Non-detectable- used 1/2 MDL, (MDL=2.7 ng/m<sup>3</sup>).

d - Corrected for 80% field recoveries.

<sup>\* -</sup> Arithmetic

distance from the application sites. The ambient air monitoring data from the earlier studies indicate that the period between October 1 to November 2 includes the peak exposure season for DEF. This is consistent with the results from the later studies (Kilgore, *et al.*, 1994; Seiber, *et al.*, 1988). The later studies with improved technical capability contain the data that more clearly present the concentration of DEF in the ambient air of residential areas close to cotton fields in California. The later studies are used in the following section to estimate public exposure to DEF in California.

## VI. ESTIMATE OF PUBLIC EXPOSURE TO DEF IN CALIFORNIA

The data suggest that residents of rural cotton growing areas may be exposed to airborne DEF during the cotton defoliation season. The absorbed dosage per unit of body weight varies between children, adult females, and adult males because the ratio of inhalation rate to the body weight varies from one subgroup to another. Therefore, the estimate of human exposure is separated into these three subgroups. Children of age six were chosen as the highest exposure subgroup, representing infants, children, and teenagers up to 18 years old. Children of age six have the highest inhalation rate (during rest and light activity) to the body weight ratio.

Since the level of exposure to airborne DEF depends on the rate of inhalation and the rate of inhalation varies with the human activity, the estimate of exposure for each subgroup was obtained from the inhalation rate of each subgroup during various daily (24 hours) activities. The U.S. EPA exposure factors handbook suggests an activity pattern for adults consisting of 11.2 hours of rest, 11.2 hours of light activity, 1.4 hours of moderate activity, and 0.2 hours of heavy activity during a 24-hour day (U.S. EPA, 1990). The activity pattern for children in California consists of at least 16 hours of rest during a day, and their light, moderate, and heavy activity periods are approximately 6.4, 1.4, and 0.2 hours, respectively (Phillips *et al.*, 1991).

The estimate of a single day or acute exposure to a person is expressed as the absorbed daily dosage (ADD). The 95th percentile of the airborne DEF concentrations at each location during the entire season is used to calculate a single day exposure. Seasonal exposure to a person is expressed as seasonal average daily dosage (SADD). The mean (arithmetic) airborne DEF level during the entire season at each location is used to calculate a SADD. A seasonal exposure period of 60 days in a year (Figure 2) was used to calculate annual exposure or annual average daily dosage (AADD).

From the data collected by Seiber *et al.* (1988), it appears that the peak exposure period in Fresno County may be from mid-September to mid-October but significant exposure may exist

during the entire season in September and October (Figure 2). The estimates of ADD, SADD, and AADD for persons in Fresno County are shown in Table 5.

Table 6. Estimates of DEF Concentration in Ambient Air and Public Exposure in Four Rural Areas in Fresno County Based on Seiber *et al.* (1988) Data

	Five Points	Tranquility	San Joaquin	Huron	Average
	$ng/m^3$	$\underline{ng/m}^3$	$\underline{ng/m}^3$	$\underline{ng/m}^3$	$\underline{ng/m}^3$
95th percentile	449.0	280.0	205.0	116.0	243.0
Seasonal Mean	182.0	112.0	75.8	43.9	104.0
Seasonal SD	163.0	102.0	78.7	44.1	84.3
	(ng/kg/day)	(ng/kg/day)	(ng/kg/day)	(ng/kg/day)	(ng/kg/day)
ADD (Child)	304.0	189.0	139.0	78.6	164.0
ADD (Adult male)	126.0	78.3	57.5	32.6	68.0
ADD (Adult female)	94.2	58.6	43.1	24.4	50.9
SADD (Child)	123.0	75.7	51.3	29.7	70.2
SADD (Adult male)	50.8	31.4	21.2	12.3	29.1
SADD (Adult female)	38.1	23.5	15.9	9.2	21.8
AADD(Child)	20.2	12.4	8.4	4.9	11.5
AADD(Adult Male)	8.4	5.2	3.5	2.0	4.8
AADD(Adult Female)	6.3	3.9	2.6	1.5	3.6

#### Based on:

Daily activity pattern of 11.2, 11.2, 1.4, and 0.2 hours of rest, light, moderate, and heavy activities, respectively, for adults (U.S. EPA, 1990); and 16.0, 6.4, 1.4, 0.2 hours of rest, light, moderate, and heavy activities, respectively, for children (Phillips *et al.*, 1991).

Inhalation rates of 0.4, 0.8, 2.0, and 2.4 m<sup>3</sup>/hour during rest, light, moderate, and heavy activities and body weight of 21.9 kg for a six-year old child (U.S. EPA, 1990). Inhalation rates of 0.7, 0.8, 2.5, and 4.8 m<sup>3</sup>/hour during rest, light, moderate, and heavy activities, respectively, and body weight of 75.9 kg for an adult male (Thongsinthusak, *et al.*, 1993). Inhalation rates of 0.4, 0.5, 1.6, and 2.9 m<sup>3</sup>/hour during rest, light, moderate, and heavy activities, respectively, and body weight of 61.5 kg for an adult female (Thongsinthusak, *et al.*, 1993).

A 100% inhalation uptake and inhalation absorption rate was assumed for airborne DEF (Assuming all airborne DEF as particulates). A seasonal exposure period of 60 days in a year was used to calculate AADD.

#### Calculation Example:

 $ADD = UC \times sum \text{ of } (IR \times DE) / BW$ 

SADD = MC x sum of (IR x DE) / BW

 $AADD = (SADD \times 60) / 365$ 

UC - upper 95% ambient air concentration (ng/m<sup>3</sup>)

MC - Mean ambient air concentration (ng/m<sup>3</sup>)

IR - inhalation rate (m<sup>3</sup>/hr)

DE - hours of daily activity (hr/day)

BW - body weight (kg)

Although Kilgore *et al.* (1984) data did not show daily airborne DEF concentration during the entire defoliation season in Kern County, the preapplication and postapplication data suggest an exposure period starting mid-September and ending early November with peak exposure period throughout the month of October. This is consistent with the data collected in Fresno County (see Figure 2) where a two-month seasonal exposure is expected. A single day public exposure (ADD) in the six rural Kern County and four urban Bakersfield areas was estimated based on the 95th percentile of the airborne DEF concentrations during and one week after the peak application season (Table 6). Public seasonal exposure (SADD) at the six rural Kern County and four urban Bakersfield areas was estimated based on the average DEF concentration during and one week after the peak application season (Table 6). This is a very conservative estimate since the average does not include DEF concentrations during the beginning and end of the season when airborne DEF levels are expected to be lower. It was assumed that airborne DEF was in particulate phase and was absorbed 100% through inhalation. This is also very conservative because airborne DEF was in both particulate and vapor phases and the vapor uptake of semivolatile chemicals rarely exceeds 75% (Raabe, 1988).

Table 7. Estimates of DEF Concentration in Ambient Air and Public Exposure in Rural Kern County and Urban Bakersfield Based on Kilgore *et al.* (1984) Data.

	Rural Kern County*	Urban Bakersfield*
	ng/m <sup>3</sup>	ng/m <sup>3</sup>
95th percentile	77.3	41.3
Seasonal Mean	33.7	25.7
Seasonal SD	26.5	9.5
	(ng/kg/day)	(ng/kg/day)
ADD (Child)	52.2	27.9
ADD (Adult male)	21.7	11.6
ADD (Adult female)	16.2	8.7
SADD (Child)	22.8	17.4
SADD (Adult male)	9.4	7.2
SADD (Adult female)	7.1	5.4
AADD(Child)	3.7	2.9
AADD(Adult Male)	1.6	1.2
AADD(Adult Female)	1.2	0.9

ADD, SADD, and AADD are based on the same factors used in Table 5.

<sup>\* -</sup> The average of the morning and evening samples.

Both adults and children spend more than 85% of their day indoors (U.S. EPA, 1990). In California, children under 12 years of age spend more than 85% of a day indoors (Phillips *et al.*, 1991). The public exposure to DEF in this document was estimated assuming the DEF concentration is the same indoors and outdoors. This assumption may provide several fold overestimation of exposure since studies have shown that the indoor ambient concentrations of tested volatile organic chemicals were up to eight fold less than those outdoors (Sheldon, *et al.*, 1992).

While it is evident that the general population residing in close proximity of cotton growing areas of California are exposed to DEF in the air through the inhalation route, the potential for exposure through the dermal route can not be ruled out. However, there are no studies available that monitored dermal exposure of the general public to airborne DEF. Studies with pesticide have shown that clothing can serve as a protective barrier against dermal exposure. Clothing can reduce any dermal exposure to DEF in the air by several fold. Thongsinthusak, *et al.* (1993) have suggested a default dermal exposure protection value of 10 fold or 90% for a long-sleeved shirt and long pants. In addition, human skin can serve as another layer of protection. A dermal absorption study of DEF in rats showed a dermal absorption rate of approximately 48% in treated animals (Schroeder, 1992); but it has been shown that human dermal absorption rates are typically several fold lower than those observed in animals, including rats (Wester and Maibach, 1993).

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